

OST TECHNICAL PROGRESS REPORT TEAM WORK PLAN--FY 2001 RESULTS

TITLE: Novel Methods of Sulfur Removal

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DESCRIPTION: Stringent fuel sulfur restrictions are likely to be imposed in the next few years. This task seeks to develop new approaches to reduce fuel sulfur in refinery streams in a manner that requires minimal new capital investment or added operating costs. Ideally, these approaches would require little additional energy input (e.g., high reactor temperatures, pressures) and have no major added energy losses (e.g., extra hydrogen consumption) during operation.

RESEARCH OBJECTIVES: Three sub-tasks were proposed to attack the sulfur problem in different ways. Sub-task one attempted to extend newly developed “green” chemistry to the problem of fuel sulfur. Sub-task two, in contrast, is directed at expanding the supply of clean fuel stocks by allowing conversion of the already ultra-clean Fischer-Tropsch waxes to a liquid fuel. A principal goal of sub-task two is to generate sufficient product to allow thorough fuel characterization.

LONG TERM GOALS / RELATIONSHIP TO NETL’S PRODUCT LINE(S): This work falls within the Transportation Fuels and Chemicals Product Team. A principal program driver is clearly environmental – developing technologies to make fuels that reduce vehicle emissions and that are compatible with the existing liquid fuel infrastructure. The Clean Air Act of 1990 directed the EPA to set standards for emissions and fuels to reduce the environmental pollution in the United States. The EPA has proposed a new set of fuel standards for fuels and emissions to be phased in beginning in 2007. The new standard for fuel includes a reduction of sulfur to a maximum of 15 ppm at the pump by June 1, 2006. The current typical fuel now has 300 ppm sulfur. There is a clear need for additional desulfurization capacity in existing refineries. An ideal solution would require (A) little additional capital investment; (B) little additional operating expense; and (C) little initial need to integrate the added desulfurization capacity within the extremely complex refinery but added as a finishing process step for existing product streams. An additional approach to reducing the sulfur levels in current fuel supplies would be to develop new sources of clean fuels, in essence diluting the sulfur levels in overall fuel stocks. The proposals investigated address these issues.

SUMMARY ACCOMPLISHMENTS: Subtask one - “Green Chemistry”: Under the University Partnership Program with Carnegie Mellon University, we have been investigating the use of tetraamidomacrocyclic ligand (TAML[®]) oxidation activators as possible candidates for a highly selective catalyst for the oxidative desulfurization of petroleum sulfur compounds. An effective catalyst structure was identified during the year. Experiments showed that the catalyst is able to oxidize several model refractory thiophenic compounds, including 4,6-dimethyldibenzothiophene, to their corresponding sulfones quantitatively at 60 °C in less than 6 minutes using hydrogen peroxide as the oxidant. Reactions were carried out in a water/alcohol solvent system.

Subtask two – Fischer-Tropsch Product Upgrading and Characterization: The team installed a

catalyst injection system on the 1-liter slurry unit, and two production runs were completed. Attempts to hydrocrack material in a trickle bed reactor system with a proprietary catalyst were partially successful. We tested straight Drakeol and began a Drakeol/wax material. This combination revealed pumping problems. Personnel recognized that a major modification to the system was required and is currently in progress. Personnel identified laboratories with the appropriate capabilities to perform the necessary ASTM analysis, and samples of straight oil and wax have been analyzed.

RESULTS: Subtask one: We have developed a series of iron (III) complexes, called TAML[®] activators, that enhance the oxidizing ability of hydrogen peroxide at low catalyst concentration and mild reaction conditions. Their versatility as oxidants lead to their use in the current study where it was found that they are capable of rapidly oxidizing the dibenzothiophene derivatives that are of concern to the petroleum industry. The general structure of TAML activators is shown in Figure 1. The R and X groups are used to control activator reactivity, selectivity, and lifetime. The activator used for this study has R=H and X=F and is referred to as FeF₂B.

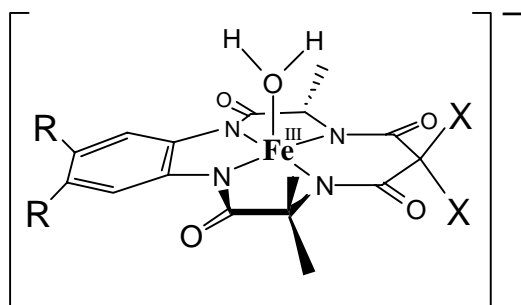


Figure 1: Structure of TAML activators

A wide range of benzothiophenes and dibenzothiophenes are rapidly oxidized by hydrogen peroxide at atmospheric pressure in the presence of the Fe-TAML activator, FeF₂B (see Figure 1) in water/tert-butanol to give the corresponding sulfone. These conversions, which generally require less than one hour, are accomplished with molar ratios of substrate to catalyst of approximately 7000:1 and a reaction temperature of 60 °C. Since the sulfones are, like the starting DBTs, very insoluble in water-rich mixtures, they precipitate from solution upon cooling to near room temperature.

The data presented in Table 1, which are preliminary kinetic measurements, reflect reactions carried out at 40 °C. These conditions are chosen to facilitate the ongoing kinetic studies and the ability to obtain high quality data. The data correspond to the reaction times to achieve greater than 95% conversion of the DBT derivative to the sulfone as determined by UV/visible spectroscopy. The differences between the starting DBT derivative and its corresponding sulfone are significant enough that this is readily determined. The overall efficiency of the oxidation process, the reaction rates, and the reaction pathways are still under investigation. It is worthwhile to note that increasing the temperature to 60 °C and raising the FeF₂B concentration to 1.5 μM (0.25 μM for kinetic studies) results in the oxidation of 4,6-dimethyldibenzothiophene (approx. 80 μM, 17 ppm) in less than 1 minute as determined by UV/vis measurements. Thus the oxidation of the thiophenes is extremely

rapid with this catalyst system.

Table 1. Reaction times of DBT derivatives at 40°C.^a

| Compounds ^b | Reaction Time (sec) |
|------------------------------|------------------------|
| | >95% conversion |
| Dibenzothiophene | 200 |
| 4-Methyldibenzothiophene | 1500 |
| 2-Methyldibenzothiophene | 800 |
| 4,6-dimethyldibenzothiophene | 150 |
| 1,2-Benzophenylenesulfide | >8000 |

^aFeF₂B concentration 0.25 μM

^bCompound concentrations approximately 80 μM

A new method to reduce sulfur content in petroleum is needed to meet future regulations. The results presented here indicate that the Fe-TAML activators of H₂O₂ are capable of rapidly oxidizing the dibenzothiophene derivatives present in fuels under mild reaction conditions. The results further indicate that an ODS process with Fe-TAML activators is a promising technology for decreasing sulfur content in fuels, especially since these are non-corrosive.

Subtask Two:

Trickle Bed

Preliminary hydrocracking tests with (1) Drakeol and with (2) Drakeol and SASOL F-T wax using a commercially available catalyst were initiated. Results from these initial experiments are shown in Table 2.

| Table 2: Hydrocracked Product Characterization | | | | | | |
|---|---------|------------|--------|--------|-----------|-------|
| | Drakeol | F-T Wax | DO 315 | DO 343 | DO-FT 343 | DO-FT |
| IBP °F | 580 | 601 | 360 | 540 | | |
| 10% | 648 | 753 | 616 | 624 | | |
| 30% | 674 | 875 | 657 | 656 | | |
| 50% | 694 | 1001 | 683 | 676 | | |
| 70% | 715 | | 714 | 704 | | |
| 90% | 732 | | 736 | 717 | | |
| End Point | 732 | | 742 | 717 | | |
| Viscosity @ 20 °C | 44.82 | No Flow | 40.99 | 45.63 | | |
| Viscosity @ 100 °C | 3.84 | No Flow | 3.66 | 3.9 | | |
| Density @ 20 °C | 0.8574 | Not Liquid | 0.8518 | 0.8533 | | |
| Density @ 100 °C | 0.8072 | 0.787 | | | | |
| Carbon, wgt % | 83.13 | 82.28 | 82.34 | 83.92 | | |
| Hydrogen, wgt % | 13.6 | 14.26 | 13.87 | 13.72 | | |
| Weight Percent: | | | | | | |
| Paraffins | 50 | 87.3 | 39.7 | 37.3 | 37.7 | 38.8 |
| Monocycloparaffins | 27.8 | 11.3 | 36.4 | 32.2 | 32.8 | 34.8 |
| Dicycloparaffins | 17.5 | 1.3 | 14.5 | 17.8 | 16.5 | 15.6 |
| Tricycloparaffins | 4.7 | 0.1 | 9.4 | 12.7 | 13 | 11 |
| Olefins | <0.5 | 12.7 | <0.5 | <0.5 | <0.5 | 1.3 |

Notes:

DO means Drakeol

FT means Fischer Tropsch SASOL Wax

Number is the temperature of the reactor in °C

Preliminary results indicate that the Drakeol is not hydrocracked at the conditions investigated in these experiments. Additional testing and characterization will be performed to determine if this is indeed the case.

Production Runs:

Two production runs were conducted in the 1-liter autoclave Fischer-Tropsch reactor system. Test conditions and results are shown in Table 3. The products recovered will be segregated, distilled, hydrocracked, and characterized.

| Table 3: Fischer-Tropsch Production Runs Summaries | | |
|---|----------------------------------|----------------------------------|
| FT Run Number | S3-43 | S3-44 |
| Catalyst | NETL Developed Iron based | LaPorte I Catalyst |
| Synthesis Run Conditions Flow Temperature Pressure | 1.965 SCFH 265 °C 175 psig | 1.967 SCFH 265 °C 175 psig |
| Run Duration (Hours) | 432 | 384 |
| Reactor Wax Produced | 680 grams | 1403 grams |
| Hot Trap Wax Produced | 85 grams | 123 grams |
| Oil Produced | 850 grams | 765 grams |
| Water Produced | 174 grams | 213 grams |

Notes:

Both of the runs used Sasol solid wax as the startup wax.

Activation conditions for both runs were at 270 °C and 5 psig, and flow rates were 1.965 and 1.967 SCFH, respectively, for runs S3-43 and S3-44.

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